

Pressure studies on two discotic liquid crystals

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Abstract. Pressure-temperature diagrams have been studied for two discotic compounds, hexa-*n*-octyloxytriphenylene and hexa-*n*-decanoyloxytriphenylene, both of which exhibit the columnar (*D*) phase at atmospheric pressure. Two interesting results, common to both compounds, have been obtained: (a) in contrast to what is usually observed in liquid crystals of rod-like molecules, the columnar-isotropic (*D-I*) transition, which is enantiotropic at atmospheric pressure, becomes monotropic at high pressures; (b) $dT/dP \approx 0$ for the *D-I* transition, implying that despite the drastic change in the molecular order at this transition, the associated volume change is extremely small.

Keywords. Discotic liquid crystals; columnar mesophase; pressure studies; phase diagrams.

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1. Introduction

The only pressure studies on discotic systems reported so far are those carried out on benzene-hexa-*n*-alkanoates (Chandrasekhar *et al* 1979; Venkatesh 1981; see also Chandrasekhar 1982) soon after the discovery of thermotropic mesomorphism in these compounds (Chandrasekhar *et al* 1977). In this communication we present the pressure-temperature (*P-T*) diagrams of two more discotic compounds, hexa-*n*-octyloxytriphenylene (hereafter abbreviated as HOT) and hexa-*n*-decanoyloxytriphenylene (HDOOT).

2. Experimental

The chemical structures of HOT and HDOOT are shown in figure 1. The temperatures as well as the heats of transitions of our samples were in good agreement with those reported by Destrade *et al* (1979, 1981). The pressure studies were conducted using a high pressure optical cell with sapphire windows (Kalkura 1982; Kalkura *et al* 1983). This being a direct pressure transmitting cell, the sample, sandwiched between two optically polished sapphire cylinders, was isolated from the pressure transmitting fluid (Plexol) by an elastomer material (fluran). Transitions were detected by the optical transmission technique. The intensity of laser light transmitted by the sample was monitored by a photodiode. The experiments were always conducted along isobars, i.e., pressure was kept constant and the temperature of the sample varied at a controlled

rate of about $1^{\circ}\text{C}/\text{min}$. At the phase transition there was an abrupt change in the transmitted light intensity. Pressure was measured (using a Heise gauge) to an accuracy of ± 1.5 bar and the temperature to $\pm 0.1^{\circ}\text{C}$.

3. Results and discussion

The P - T diagrams are shown in figures 2 and 3. The following features are common to both diagrams. The crystal (K)-columnar (D) phase transition temperature increases steeply with increasing pressure while the D - I transition temperature is practically independent of pressure. This results in a rapid diminution of the temperature range of existence of the D phase in the P - T plane. Ultimately the K - D and D - I lines intersect, resulting in a K - D - I triple point. These triple points (which were obtained by recording the transitions in the heating mode) occur at 0.64 kbar, 84.5°C for HOT and at 1.25 kbar,

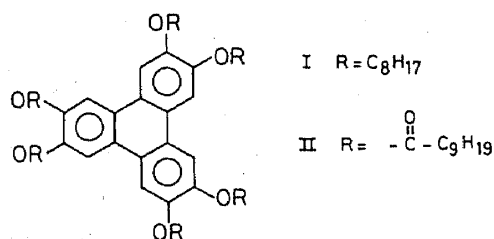


Figure 1. Chemical structures of the compounds studied: (I) hexa-*n*-octyloxytriphenylene (HOT) and (II) hexa-*n*-decanoyloxytriphenylene (HDOOT).

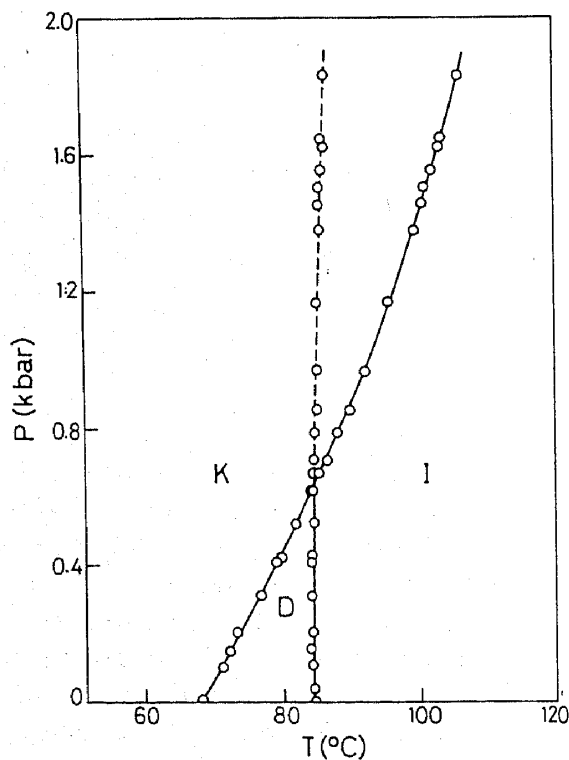


Figure 2. Pressure-temperature diagram of hexa-*n*-octyloxytriphenylene.

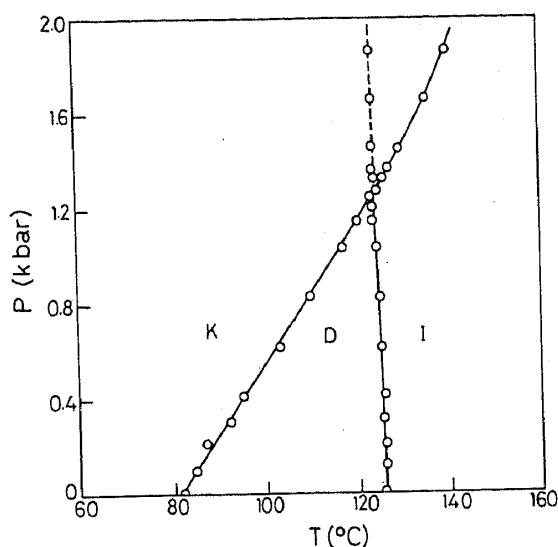


Figure 3. Pressure-temperature diagram of hexa-*n*-decanoyloxytriphenylene.

123°C in the case of HDOOT. Beyond the pressure corresponding to the triple point, the discotic phase is seen only on cooling from the isotropic phase. In other words, the character of the *D-I* transition changes from enantiotropic to monotropic. Except in the special case of reentrant systems (Cladis *et al* 1978; Kalkura *et al* 1983) this is the reverse of what is observed in liquid crystals of rod-like molecules wherein a monotropic transition becomes enantiotropic at high pressures (Shashidhar 1977; Chandrasekhar and Shashidhar 1979).

Another noteworthy aspect of the *P-T* diagrams is that for both compounds, dT/dP for the *D-I* transition is nearly equal to zero over the entire range of pressure investigated. Cases are known in rod-like reentrant nematogenic systems of the slope of the smectic *A*-nematic phase boundary being zero over a very small pressure range before becoming negative (Cladis *et al* 1978; Kalkura *et al* 1983). However, as far as we are aware, these appear to be the only instances of the slope of the mesophase-isotropic transition being nearly zero over such a large pressure range. Considering that the heat of the *D-I* transition is quite large, 1.04 kcal/mole for HOT and 0.69 kcal/mole for HDOOT, this result is somewhat surprising and implies that the volume change associated with the *D-I* transition should be negligibly small. We are undertaking accurate density measurements to ascertain this point.

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